



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 551 525 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: **92916524.9**

(51) Int. Cl.⁵: **G01N 27/07**

(22) Date of filing: **31.07.92**

(86) International application number:
PCT/JP92/00974

(87) International publication number:
WO 93/03354 (18.02.93 93/05)

(30) Priority: **06.08.91 JP 196528/91**

(43) Date of publication of application:
21.07.93 Bulletin 93/29

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: **SHINAGAWA REFRACTORIES CO., LTD.**
2-1, Ohtemachi 2-chome Chiyoda-ku
Tokyo 100(JP)

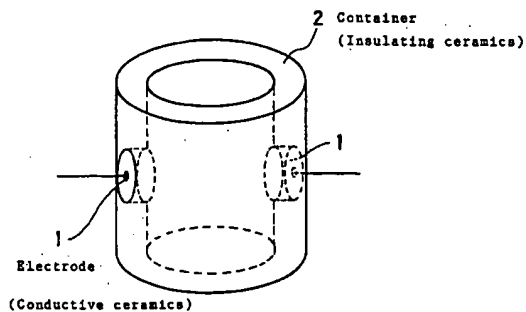
(72) Inventor: **SHIRANITA, Akira**
18-39, Jotoh-Kitagata
Okayama-shi, Okayama 709-08(JP)
Inventor: **NAKAYAMA, Susumu**
390, Higashi-Katakami
Bizen-shi, Okayama 705(JP)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4 P.O. Box 86 07 67
W-8000 München 86 (DE)

(54) **CONDUCTIVITY MEASURING CELL.**

(57) A container part (2) and an electrode part (1) of a conductivity measuring cell are made of ceramic having high corrosion resistance, and the container part (2) is made of insulating ceramic and the electrode part (1) is made of a conductive ceramic having a resistance value of up to several kilo-ohms.centimeters. Ceramic has by far higher corrosion resistance and mechanical strength at both normal and high temperatures than glass and is more inexpensive than precious metals. It can be used under the presence of strong acids and alkalis, can be used under high pressures and at high temperatures, and can further reduce the cost.

Fig. 2



TECHNICAL FIELD

The present invention relates to a cell for measuring electrical conductivity of liquid having conductivity of $100 \text{ k}\Omega \cdot \text{cm}$ or less, and in particular to a cell for measuring conductivity, which can be used at high temperature or high pressure conditions and in corrosive substances by adopting ceramics for container and electrodes.

BACKGROUND TECHNIQUE

In the past, a cell as shown in Fig. 1 has been used for measuring electrical conductivity of liquid having conductivity of $100 \text{ k}\Omega \cdot \text{cm}$ or less.

Fig. 1 (a) shows a cell, which comprises a glass container 2 with side tubes 4 protruding inwardly on the sides thereof, electrodes 1 made of precious metal such as platinum and supported on tips of the side tubes, and lead wires 5 passed through the side tubes.

Specimen liquid 6 is placed in the container and a stopper 3 is provided to close it, and electric current is applied across the electrodes to measure electrical conductivity.

Fig. 1 (b) shows a filling type cell for laboratory use. On both ends of an oblong glass container 2, electrodes 1 are disposed, and specimen liquid is filled through and discharged from two side tubes 7a and 7b extending upward. By applying electric current across the electrodes on the two ends of the glass container 2, electrical conductivity is measured.

Fig. 1 (c) shows an immersion type cell. A glass container 2 has a small opening. By immersing the container in specimen liquid, the liquid enters through the opening. Electrical conductivity is measured by applying electric current across the electrodes.

However, each of the conventional type cells has problem in corrosion resistant property, particularly against alkali, because glass is used for the container. Also, there are problems with mechanical strength and corrosion resistant property under high temperature and high pressure conditions. If metal other than precious metal is used for electrodes, problems arise with corrosion resistant property. The use of precious metal leads to the increase of cost because Pt, Au, etc. are expensive.

It is an object of the present invention to provide a cell, which has high corrosion resistant property and can be used under strong acid or strong alkaline conditions.

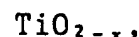
It is another object of the present invention to provide a cell, which has high mechanical strength and is suitable for the use under high pressure and high temperature conditions.

It is still another object of the present invention to provide a cell, which can be produced at lower cost.

DISCLOSURE OF THE INVENTION

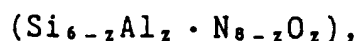
To attain the above objects, the cell for measuring conductivity according to the present invention uses ceramics with high corrosion resistant property for container and electrodes, whereby the container is made of insulating ceramics, and electrodes are made of conductive ceramics having resistance value of several $\text{k}\Omega \cdot \text{cm}$ or less.

As ceramic materials for electrodes, there are carbides such as TiC, ZrC, VC, TaC, Mo_2C , WC, SiC, etc., nitrides such as TiN, ZrN, VN, NbN, TaN, Cr_2N , etc., carbonitride Ti(C-N), borides such as TiB_2 , ZrB_2 , NbB_2 , TaB_2 , CrB_2 , MoB, etc., silicides such as TiSi_2 , ZrSi_2 , NbSi_2 , CrSi_2 , MoSi_2 , WSi_2 , etc., single conductive ceramic such as



conductive material such as complex ceramics containing two or more types of these substances, oxynitrides type sialon (a series of substances containing elements of Si-Al-O-N), and complex ceramics with Al_2O_3 , ZrO_2 , etc.

As the ceramic materials to be used for the container, there are various types of insulating ceramics such as Si_3N_4 , α -sialon $(\text{Y}_x(\text{Si}, \text{Al})_{1-2}(\text{O}, \text{N})_1)_\epsilon$, β -sialon



ZrO_2 , Al_2O_3 , mullite, spinel, SiC, etc.

With the materials selected from these substances, a cell in cylindrical shape is prepared as shown in Fig. 2. In Fig. 2, the reference numeral 1 represents an electrode made of conductive ceramics, 2 is a container made of insulating ceramics, and the electrodes are provided on the sides of the container. To produce such cell, there are various methods such as a method to integrally mold two types of powder materials for container and electrodes and to fabricate and fire, a method to mold the container and the electrodes separately and then to combine them and to fire, a method to mold and fire the container and the electrodes separately and bond with glass-frit having high corrosion resistant property.

The present invention provides a cell for conductivity measurement, which comprises container and electrodes made of ceramics. The ceramics are much superior to glass in corrosion resistant

property and mechanical strength under normal as well as high temperature conditions and are less expensive than precious metal. Therefore, the cell for measuring conductivity of the present invention has high corrosion resistant property and can be used under strong acid or strong alkaline conditions. It is also suitable for the use under high pressure and high temperature conditions because it has high mechanical strength. Further, it can be produced at low cost because precious metal is not used for the electrodes. The junction between the container and the electrodes has airtightness as high as 10^{-7} Torr or more by He leakage test, and there is no possibility of liquid leakage.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates conventional type cells for measuring conductivity;

Fig. 2 shows a cell for measuring conductivity of the present invention;

Fig. 3 shows the results of chemical resistance test;

Fig. 4 summarizes mechanical property of the materials; and

Fig. 5 shows electric resistance values of the materials.

BEST MODES FOR CARRYING OUT THE INVENTION

Fig. 2 represents an embodiment of a cell for measuring conductivity according to the present invention. α -sialon is used as insulating ceramics for the container portion 2. As conductive ceramics for the electrodes 1, (1) TiN-dispersed α -sialon, (2) TiC-dispersed α -sialon, and (3) SiC-dispersed α -sialon are used. To prepare raw material powder for the insulating α -sialon, Si_3N_4 , Y_2O_3 and AlN were blended by weight ratio of 91 : 5 : 4, and the mixture was kneaded in a ball mill for 48 hours with ethanol and was dried. The raw material powder of conductive α -sialon-TiN in (1) above was prepared by blending Si_3N_4 , Y_2O_3 , AlN and TiN by weight ratio of 54 : 3 : 2 : 41, the raw material powder of the conductive α -sialon-TiC of (2) above was prepared by blending Si_3N_4 , Y_2O_3 , AlN, TiC and Al_2O_3 by weight ratio of 54 : 3 : 2 : 40 : 1, and the raw material powder of the conductive α -sialon-SiC of (3) above was prepared by blending Si_3N_4 , Y_2O_3 , AlN, SiC and carbon black by weight ratio of 54 : 3 : 2 : 40 : 1. Each of these mixtures was kneaded in a ball mill for 48 hours with ethanol and was dried. The raw material powder thus prepared was processed by CIP molding at 1,000 kg/cm² and was fired for 2 hours at 1,600 - 1,950 °C in nitrogen atmosphere to produce sintered substance. The results of chemical resistance test,

mechanical property, and electric resistance values of each of the sintered substances of α -sialon, (1) α -sialon-TiN, (2) α -sialon-TiC, and (3) α -sialon-SiC are given in Fig. 3, Fig. 4 and Fig. 5 respectively.

Fig. 3 shows the results of chemical resistance test. When the materials were exposed to H_2SO_4 , HCl, HNO_3 (concentration: conc. and 10%; temperature: 80 °C), HF (room temperature), and NaOH (concentration: 50%; temperature: 80 °C), weight decrease (mg/cm² · day) was slight, and it is evident that each of these materials has very high corrosion resistant property.

Fig. 4 gives 3-point modulus of rupture (kg/mm²) and fracture toughness (MN/m^{1/2}) of container material (insulating ceramics) and electrode material (conductive ceramics). It is evident that the materials have very high mechanical strength.

Fig. 5 shows electric resistance values ($\Omega \cdot \text{cm}$) of the materials. From the figure, it is evident that the container material has resistance value as high as 10^{12} or more, while the electrode material has resistance of 10 or less, showing excellent conductivity. The resistance value may be less than several k $\Omega \cdot \text{cm}$.

[Example 1]

Each of the raw material powders of α -sialon, (1) α -sialon-TiN, (2) α -sialon-TiC, or (3) α -sialon-SiC was processed by CIP molding under pressure of 500 - 1,000 kg/cm². Then, as shown in Fig. 2, α -sialon material was molded into the shape of the container, the materials of (1) α -sialon-TiN, (2) α -sialon-TiC, and (3) α -sialon-SiC were molded into the shape of electrodes, and these were combined together. By sintering the base materials for 2 hours at 1,600 - 1,950 °C in nitrogen atmosphere, the cell for conductivity measurement was obtained. The container and the electrodes were bonded closely without gap, and airtightness was as high as 10^{-7} Torr or more by He leakage test.

[Example 2]

Each of the raw material powders of α -sialon, (1) α -sialon-TiN, (2) α -sialon-TiC, or (3) α -sialon-SiC was processed by CIP molding under pressure of 1,000 kg/cm². Then, as shown in Fig. 2, α -sialon material was molded into the shape of the container, and the materials of (1) α -sialon-TiN, (2) α -sialon-TiC, or (3) α -sialon-SiC were molded into the shape of electrode, and these were sintered for 2 hours at 1,600 - 1,950 °C in nitrogen atmosphere. The sintered materials thus obtained were fabricated in such manner that clearance was 0.1 mm or less when the container and the electrodes were assembled and bonded at 1,000 °C in nitrogen

atmosphere using glass having high chemical resistance such as borosilicate frit or titanium frit. The cell thus obtained showed airtightness as high as 10^{-7} Torr or more between the container and the electrodes by He leakage test, similarly to Example 1.

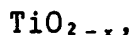
sialon, ZrO_2 , Al_2O_3 , mullite, spinel, SiC, etc.

INDUSTRIAL APPLICABILITY

As described above, the cell for measuring conductivity according to the present invention has high corrosion resistant property and is suitable for the use under strong acid or strong alkaline conditions. Because it has high mechanical strength, it can be used under high pressure and high temperature conditions. Further, it can be produced at low cost because precious metal is not used for the electrodes. Thus, the cell is very valuable in industrial applications.

Claims

1. A cell for measuring electrical conductivity of a specimen by putting the specimen into a container provided with electrodes and by applying electric current across the two electrodes, whereby the container and the electrodes are made of ceramics.
2. A cell for measuring electrical conductivity according to Claim 1, wherein the container is made of insulating ceramics, and the electrodes are made of conductive ceramics having resistance value of several $k\Omega \cdot cm$ or less.
3. A cell for conductivity according to Claim 2, wherein the conductive ceramic materials contain carbides such as TiC, ZrC, VC, TaC, Mo_2C , WC, SiC, etc., nitrides such as TiN, ZrN, VN, NbN, TaN, Cr_2N , etc., carbonitride Ti (C-N), borides such as TiB_2 , ZrB_2 , NbB_2 , TaB_2 , CrB_2 , MoB, etc., silicides such as $TiSi_2$, $ZrSi_2$, $NbSi_2$, $CrSi_2$, $MoSi_2$, WSi_2 , etc., single conductive ceramic such as



conductive materials such as complex ceramics containing two types or more of these substances, and complex ceramics with Si_3N_4 , sialon, Al_2O_3 , ZrO_2 , etc.

4. A cell for measuring electrical conductivity according to Claim 2, wherein the insulating ceramic material contains various types of ceramic material such as Si_3N_4 , α -sialon, β -

Fig. 1

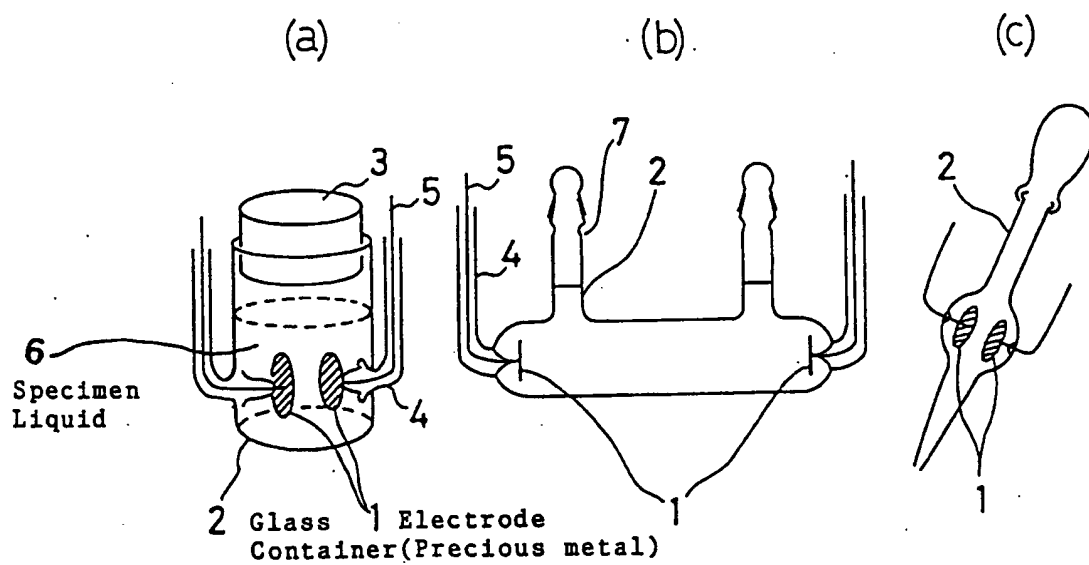


Fig. 2

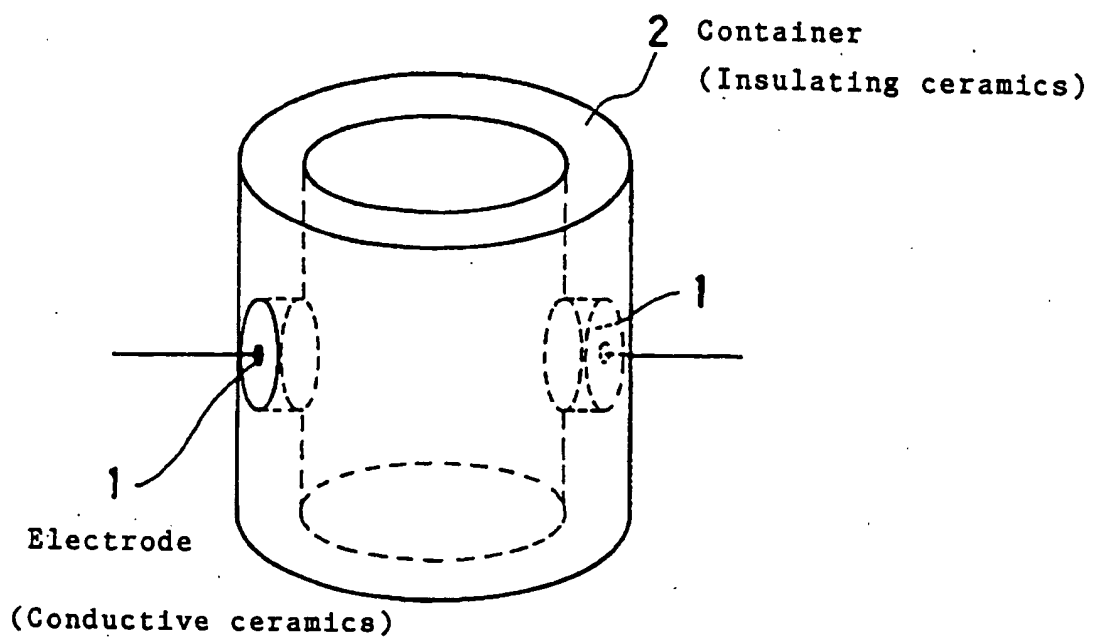


Fig. 3

Conditions		Container material (insulating ceramics)	Electrode material (conductive ceramics)		
Chemicals	Temperature		① α -Sialon-TiN	② α -Sialon-TiC	③ α -Sialon-SiC
H ₂ SO ₄ (conc.)	80 °C	0.04	- 0.47	- 0.04	0.01
H ₂ SO ₄ (10%)	80 °C	0.82	1.05	1.11	0.30
HCl (conc.)	80 °C	0.37	2.55	2.20	0.52
HCl (10%)	80 °C	0.57	2.35	2.10	0.51
HNO ₃ (conc.)	80 °C	0.14	0.54	0.72	0.02
HNO ₃ (10%)	80 °C	0.55	4.53	3.23	0.81
HF (5%)	Room Temp.	0.33	0.78	0.84	0.25
NaOH (50%)	80 °C	0.07	0.01	0.02	0.00

Unit: Weight decrease (mg/cm² · day)

Fig. 4

		3-point modulus of rupture (kg/mm ²)	Fracture toughness (MN/m ^{3/2})
Container material (insulating ceramics)	α -Sialon	100	6
Electrode material (conductive ceramics)	① α -Sialon-TiN	75	5
	② α -Sialon-TiC	75	6
	③ α -Sialon-SiC	80	5

Fig. 5

		Electric resistance ($\Omega \cdot \text{cm}$)
Container material (insulating ceramics)	α -Sialon	10^{12} or more
Electrode material (conductive ceramics)	① α -Sialon-TiN	10^1 or less
	② α -Sialon-TiC	10^3 or less
	③ α -Sialon-SiC	10^3 or less

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/00974

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵ G01N27/07		
II. FIELDS SEARCHED		
Minimum Documentation Searched ¹		
Classification System	Classification Symbols	
IPC	G01N27/06-27/10, 27/28, 27/30	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
Jitsuyo Shinan Koho 1926 - 1992 Kokai Jitsuyo Shinan Koho 1971 - 1992		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	JP, A, 59-84148 (Toyobo Co., Ltd.), May 15, 1984 (15. 05. 84), (Family: none) Particularly refer to lines 7 to 14, lower right column, page 2	1-5
A	JP, Y, 62-3145 (Kimura Shindai Kogyo K.K.), January 24, 1987 (24. 01. 87), (Family: none)	1-5
A	JP, A, 1-244355 (Toshiba Corp.), September 28, 1989 (28. 09. 89), (Family: none)	2, 3
<p>* Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
October 14, 1992 (14. 10. 92)	November 2, 1992 (02. 11. 92)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		